The University of Chicago

REACTIONS OF ALUMINUM BOROHYDRIDE WITH CERTAIN CARBON COMPOUNDS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
AUGUST, 1946

By
ROBERT AUGUSTIN LAD

CHICAGO, ILLINOIS
1946

The University of Chicago

REACTIONS OF ALUMINUM BOROHYDRIDE WITH CERTAIN CARBON COMPOUNDS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
AUGUST, 1946

By
ROBERT AUGUSTIN LAD

CHICAGO, ILLINOIS
1946

R. UNIV.
BIBLIOTHEEK
LEIDEN

ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor H. I. Schlesinger, under whose able direction this work was carried out, and to Dr. M. Gerstein, Dr. A. E. Finholt and Mr. A. C. Bond who assisted with some of the experimental work.

REACTIONS OF ALUMINUM BOROHYDRIDE WITH CERTAIN CARBON COMPOUNDS

Although a number of borohydrides, such as those of the alkali metals, $LiBH_4$, of beryllium, $Be(BH_4)_2$, and of aluminum, $Al(BH_4)_3$,[1] have been prepared and characterized, relatively little has been published about their chemical reactions, except for their behavior toward water, alcohols, ethers, and tertiary amines. It is also known that they are strong reducing agents and that they undergo metathetic reactions in which the BH_4 group retains its identity. As an extension of this knowledge of their behavior we have undertaken a more systematic study of their reactions with various types of organic compounds.

This paper deals with the behavior of aluminum borohydride toward a number of alkoxy and of halogen compounds of carbon. Aluminum borohydride was chosen because it is more reactive than the alkali metal borohydrides and because it is soluble in several organic solvents; the alkoxy and halogen derivatives were selected because some as yet unpublished observations indicated that their reactions might be of special interest. Since this investigation represents a new field of inquiry, it has been made exploratory in character rather than a detailed study of one or two reactions.

Earlier as yet unpublished studies of the reactions of borohydrides had shown that, in a number of cases, these compounds

---

[1] H. I. Schlesinger and H. C. Brown, J. Am. Chem. Soc., 62, 3429 (1940); A. B. Burg and H. I. Schlesinger, ibid., 62, 3425 (1940); and H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, ibid., 62, 3421 (1940). Since the publication of these papers the borohydrides of sodium and potassium have been prepared (unpublished work).

replace halogen atoms and alkoxy groups by borohydride groups. It therefore seemed not unreasonable to attempt to interpret the reactions herein described in terms of the assumption that their first step is a replacement of this type, and that this step is followed by the loss of either a borine (BH_3) molecule or of hydrogen, or of both, from the hypothetical carbon borohydride. This treatment of the results leads to certain logical difficulties both as to the nature of the bond involved in a carbon borohydride and as to the actual course of the reactions; it is nevertheless presented because it permits a convenient classification of the reactions studied, and because it calls attention to a number of striking and unexpected differences between otherwise closely related organic compounds. It should be emphasized at once that the assumptions involved are not advanced as actual mechanisms of the reactions.

Before presenting the equations which show the products of the reactions and the classification referred to, a number of conventions employed should be mentioned. The formulae of the hypothetical intermediates are enclosed in brackets. Diborane, one of the reaction products, is represented by the formula BH_3 since doing so makes clear the postulated mode of decomposition of the assumed intermediate. A similar convention is used for the other type of product, i.e., the methyl diboranes, which are represented by the formula CH_3BH_2 instead of $(CH_3)_2B_2H_4$. In this connection attention is called to the fact that the monomer, $(CH_3)BH_2$, should polymerize to the symmetrical dimethyl diborane. Instead, the unsymmetrical compound was obtained as a reaction product, as is to be expected since the symmetrical diborane derivative rapidly undergoes rearrangement to the other.[2] Also

---

[2] H. I. Schlesinger, N. W. Flodin, and A. B. Burg, J. Am. Chem. Soc., 61, 1078 (1939).

alkyl diboranes undergo disproportionation;[3] consequently the dialkyl derivatives were contaminated with small quantities of the disproportionation products. It should also be mentioned that it was not in every case determined whether the aluminum compound obtained as a reaction product was AlX_3 or $Al(BH_4)_nX_{3-n}$. The suggested classification may now be presented and discussed.

I. The hypothetical intermediate loses only BH_3 groups. To this group belong ethyl orthoformate, methylal and chloroform:

(a) $HC(OC_2H_5)_3 + Al(BH_4)_3 \longrightarrow [HC(OC_2H_5)(BH_4)_2] + AlBH_4(OC_2H_5)_2$

$[HC(OC_2H_5)(BH_4)_2] \longrightarrow CH_3OC_2H_5 + 2BH_3$

(b) $H_2C(OCH_3)_2 + Al(BH_4)_3 \longrightarrow [H_2C(OCH_3)BH_4] + Al(BH_4)_2OCH_3$

$[H_2C(OCH_3)BH_4] \longrightarrow H_3COCH_3 + BH_3$

(c) $3HCCl_3 + Al(BH_4)_3 \longrightarrow 3[HCBH_4Cl_2] + AlCl_3$

$[HCBH_4Cl_2] \longrightarrow H_2CCl_2 + BH_3$

II. The hypothetical intermediate decomposes in two ways, i.e., by loss of BH_3 groups and by loss of hydrogen. This group includes methyl iodide, methylene fluoride, and, possibly, methylene iodide.

(a) $3CH_3I + Al(BH_4)_3 \longrightarrow 3[CH_3BH_4] + AlI_3$

$CH_3BH_4 \longrightarrow CH_4 + BH_3$

$CH_3BH_4 \longrightarrow CH_3BH_2 + H_2$

(b) $3CH_2F_2 + 2Al(BH_4)_3 \longrightarrow 3[CH_2(BH_4)_2] + 2AlF_3$

$[CH_2(BH_4)_2] \longrightarrow [CH_3BH_4] + BH_3$

$[CH_3BH_4] \longrightarrow CH_4 + BH_3$

$[CH_3BH_4] \longrightarrow CH_3BH_2 + H_2$

(c) $3CH_2I_2 + 2Al(BH_4)_3 \longrightarrow 3[CH_2(BH_4)_2] + 2AlI_3$

---

[3] H. I. Schlesinger and A. O. Walker, ibid., 57, 621 (1935).

$$\begin{cases} [CH_2(BH_4)_2] \longrightarrow [CH_3BH_4] + BH_3 \\ [CH_3BH_4] \longrightarrow CH_3BH_2 + H_2 \end{cases}$$

III. The hypothetical intermediate undergoes changes in addition to loss of BH_3 and of hydrogen. To this group belong ethylene bromide and phosgene. In both cases the reaction at a temperature just above the melting point (-65°C.) of aluminum borohydride was so violent that it was accompanied by flashes of flame. In the case of ethylene bromide no method of moderating the reaction was found; addition of the aluminum borohydride in small portions to the phosgene served to moderate the reaction somewhat. The observations may be represented as follows:

(a) $$3COCl_2 + 2Al(BH_4)_3 \longrightarrow 3[CO(BH_4)_2] + 2AlCl_3$$

$$[CO(BH_4)_2] \longrightarrow CO + 2BH_3 + H_2$$

(b) $$3C_2H_4Br_2 + 2Al(BH_4)_3 \longrightarrow 3[C_2H_4(BH_4)_2] + 2AlCl_3$$

$$[C_2H_4(BH_4)_2] \longrightarrow C_2H_6 + 2BH_3$$

$$\longrightarrow C_2H_5BH_4 + H_2$$

$$\longrightarrow (C_2H_5)BH_2 + H_2$$

In the case of ethylene bromide, methane and dimethyldiborane were obtained in addition to the products represented by the equations. It is evident that no interpretation based on mere replacement of bromine atoms by borohydride groups, and subsequent loss of borine or of hydrogen, can account for the splitting of the carbon to carbon bond. Extensive reduction at the higher temperatures resulting from the vigorous reaction is evidently involved.

IV. Compounds which do not react with aluminum borohydride at room temperature: Methylene chloride and bromide,[4] iodoform, carbon tetrachloride or carbon tetrafluoride.

---

[4]Also fails to react at 60°C.

Examination of the equations and of the facts represented by them brings out a number of points worthy of notice. From ethyl orthoformate and methylal, aluminum borohydride removes all but one of the alkoxy groups, a behavior consistent with the failure of ethers to react with the reagent (except by addition). From chloroform only one chlorine atom is removed and methylene chloride does not react at all, but this behavior is not inconsistent with that of the alkoxy derivatives, since the latter are in general more reactive than organic halides. Likewise the inactivity of the tetrahalides is in keeping with their other chemical behavior.

Comparison of these reactions with those of fluoro and iodo derivatives, however, leads to results less likely to have been anticipated. As just mentioned only one chlorine atom of chloroform is removed by the borohydride, and methylene chloride is unaffected; in contrast thereto all of the fluorine or the iodine atoms are removed from methyl iodide, from methylene iodide and from methylene fluoride. In view of the usual stability of the carbon-fluorine bond this difference between chloro and fluoro derivatives is unexpected. It could be explained by the great stability of the fluorine-aluminum bond; similar differences, readily interpreted in the same way, have been found in as yet unpublished reactions of inorganic chlorides and fluorides with aluminum borohydride.

The most serious difficulty of interpretation is that encountered in the difference in the behavior of methyl iodide and methylene fluoride on the one hand, and of methylene iodide on the other hand. The first two give methane, diborane, methyl diboranes and hydrogen; methylene iodide produces no methane. Unless further assumptions are made, this result implies that the hypothetical intermediate CH_3BH_4 decomposes both by loss of borine

and of hydrogen when it is derived from methyl iodide or from methylene fluoride, but only by loss of hydrogen when the same intermediate is derived from methylene iodide. The difficulty is avoided by the additional assumption that the first step in the reaction of aluminum borohydride with the methylene derivatives is the formation of the intermediates CH_2FBH_4 and CH_2IBH_4, respectively. The latter of these may then be supposed to lose hydrogen iodide to form CH_2BH_3 which rearranges to CH_3BH_2 (i.e., to dimethyldiborane); the formation of hydrogen and of diborane would be the result of the interaction of hydrogen iodide with aluminum borohydride. Since hydrogen fluoride is less easily lost in such reactions, the intermediate, CH_2FBH_4, might be expected to lose borine thus producing methyl fluoride, which would react further with aluminum borohydride, as does methyl iodide, to give methane, hydrogen, diborane and methyldiboranes.

No hypothesis has been offered to explain why, according to the interpretation just discussed, some of the assumed intermediates react by the loss of hydrogen and others by loss of borine or of hydrogen; at present the only clue lies in the fact that when not all of the alkoxy groups or halogen atoms are removed from the carbon compound, the products are those which would result from loss of borine alone.

It might be thought that the logical difficulties pointed out result solely from the assumption of the postulated intermediates. Obviously, however, any other mode of interpretation must encounter similar difficulties; discussion from the point of view presented merely calls attention to discrepancies in the behavior of the organic compounds studied, a discrepancy whose elucidation should be of general interest. It is apparent that a greater variety of compounds must be investigated; furthermore,

precise data on the proportions of the various reaction products at a series of temperatures will have to be secured before any further explanation of the course of such reactions can be successful. With regard to the last point only fragmentary information is as yet available. In the case of methyl iodide, 70 per cent of the carbon was found as methane and 21 per cent as methyldiboranes; at 60°C., the ratio was 65/35. In the case of methylene fluoride, one experiment gave a ratio of 54/46, another under slightly different treatment, a ratio of 57/43 at room temperature. These ratios are only approximate values since the experiments were on too small a scale for precise determinations.

EXPERIMENTAL PART

Apparatus and technique: The apparatus and techniques employed have been described in previous publications by Stock[5] and by Schlesinger and his coworkers.[6]

Source and purification of reagents: Aluminum borohydride was prepared by a new method described in the thesis of Earle Hyde, as yet unpublished. Ethyl orthoformate (Edwal), methylal (Eastman), chloroform and ethylene bromide (Merck), were treated with Drierite for 24 hours, and then distilled at atmospheric pressure; in each case a fraction with a boiling range of at most 2°C. was used. Methylene iodide (Merck), was washed with sodium thiosulfate solution and then extracted with ether. The ether solution was treated with Drierite, after which the ether was removed in vacuo and the methylene iodide twice distilled at low pressure; another sample was distilled at atmospheric pressure. Methyl iodide (Merck), was treated first with mercury, then with Drierite and finally distilled at atmospheric pressure. Methylene fluoride was obtained from Du Pont and used as received; the boiling point, as obtained by extrapolation from the vapor tension at -112°C. (11 mm) and at -54.5° (658 mm), was -51°C., in satisfactory agreement with Booth's value of -51.6°C.[7] Phosgene (commercial) was purified by condensing in the vacuum line a sample

---

[5]A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, 1933; Ber., 54A, 142 (1921).

[6]H. I. Schlesinger and A. O. Walker, J. Am. Chem. Soc., 57, 622 (1935); A. B. Burg, ibid., 56, 499 (1934).

[7]H. S. Booth, ibid., 59, 1400 (1937).

about three times as large as was to be used, and removing the most volatile third of the sample for use.

The Reaction of Aluminum Borohydride with Ethyl Orthoformate. The reaction of aluminum borohydride with ethyl orthoformate may yield either aluminum diethoxyborohydride or aluminum monoethoxyborohydride, depending on the molar ratios of the reactants.

Experiment A--Reaction to Form $AlBH_4(OC_2H_5)_2$:

$$Al(BH_4)_3 + HC(OC_2H_5)_3 \longrightarrow CH_3OC_2H_5 + B_2H_6 + AlBH_4(OC_2H_5)_2$$

A 5.86 mmol sample of ethyl orthoformate was weighed into a 300 ml reaction bulb which was equipped with a side arm for introduction into a tube opener. The reaction bulb was then attached to the vacuum line through a ground joint and stopcock. The ethyl orthoformate was frozen with liquid nitrogen and the air pumped out of the bulb. A 6.10 mmol sample of pure aluminum borohydride (vapor tension 119.5 mm at 0°C.) was distilled into the bulb, which was then sealed off the line, and allowed to warm slowly. A vigorous reaction took place between -195° and -80° with the formation of a cloud of vapor which later condensed on the walls of the bulb as a viscous liquid (very probably $Al(BH_4)_2OC_2H_5$). The material was then warmed to room temperature and allowed to stand for 24 hours. At the end of this time the liquid had disappeared and a white solid had taken its place.

The bulb was then attached to a tube opener through a picened joint and the small amount of material not condensable at -195° (0.254 mmol) was removed with a Toepler pump. This material was probably hydrogen, formed by the reaction of aluminum borohydride with traces of impurities in the ethyl orthoformate.

The volatile products condensable at liquid nitrogen temperatures were then removed from the reaction bulb by evacuation through a U-tube cooled to -195°. This process was continued for one hour, during which time the reaction bulb was kept at 60°. The material collected in the -195° bath was distilled slowly through a U-tube cooled to -140° into a U-tube at -195°. The -195° fraction (5.43 mmoles) was found to be diborane (vapor tension at -111.8°, 225 mm). The -140° fraction (5.60 mmoles) was identified as methylethyl ether by its boiling point, 64°C. at 760 mm.[8] It forms a non-volatile addition compound with aluminum borohydride--a behavior typical of ethers. The absence of B-H links was demonstrated by the fact that the compound liberated no hydrogen on treatment with water.

The non-volatile material which remained in the reaction bulb was then hydrolyzed with methanol and the resulting hydrogen removed by a Toepler pump and measured. The methanol solution was analyzed for boron in the usual manner. Aluminum was determined as the 8-hydroxy quinolate.

Complete interaction should result in the formation of 5.86 mmoles each of diborane and methylethyl ether. Since aluminum borohydride was in slight excess and since it readily forms non-volatile addition compounds with ethers, it is reasonable to assume that the excess aluminum borohydride (0.23 mmol) combined with 0.23 mmol of the ether formed in the reaction. Added to the 5.60 mmoles liberated, this gives a total of 5.83 mmoles or 99.5 per cent of theoretical. The diborane (5.43 mmoles) represents 93 per cent of theoretical; a small amount was adsorbed by the

---

[8]This is in agreement with a recent literature value of 6.6°C. for the boiling point at 760 mm, determined by V. N. Ipatieff and Robert L. Burwell, Jr., J. Am. Chem. Soc., 65, 889 (1943). The boiling point of the methylethyl ether in the above experiment was obtained by extrapolation from vapor tensions

non-volatile reaction products, as shown by the analysis of the residue. The latter should contain:

5.86 mmol $AlBH_4(OC_2H_5)_2$

0.23 mmol $Al(BH_4)_3$--excess for the reaction

0.23 mmol $CH_3OC_2H_5$--as aluminum borohydride etherate

0.43 mmol B_2H_6 not removed in the evacuation.

Analysis gave the following results:

	calculated	found
Al	6.10 mmol	6.19 mmol
B	7.42	7.27
H (hydrolyzable)	14.4	15.5

Material Balance:

	used	found
Al	6.10 mmol	6.19 mmol
B	18.29	18.13
H (not including that in C_2H_5)	42.4	40.2

Experiment B--Reaction to Form $Al(BH_4)_2OC_2H_5$:

$$2Al(BH_4)_3 + HC(OC_2H_5)_3 \longrightarrow CH_3OC_2H_5 + B_2H_6 + 2Al(BH_4)_2OC_2H_5$$

Ethyl orthoformate, 2.47 mmoles, and aluminum borohydride, 4.85 mmoles, were sealed off in the same manner as in the previous experiment. The reaction bulb in this case was constructed with a U-tube in the side arm. The reaction again took place below -80° with the formation of a cloud of white vapor which condensed on the walls of the bulb as a viscous liquid. After long standing (one week) at room temperature, the reaction bulb was connected to a tube opener by a picened joint, and opened to the vacuum line. A very small amount of gas not condensable in liquid

---

measured at lower temperatures (589 mm at 0°C., 66 mm at -45°C., and 6 mm at -80°C.).

nitrogen was found to be present. After the non-condensable gas was pumped out, a -80° bath was placed around the U-tube of the reaction vessel and the diborane and methylethyl ether were removed by evacuation through another U-tube cooled with liquid nitrogen. During the evacuation, the viscous liquid in the reaction bulb was heated with a hair dryer until it had distilled to cool portions of the bulb and into the U-tube at -80°. It was noted that a small part of the material did not distill as readily as the rest.

The quantity of diborane obtained (2.42 mmoles) agreed exactly with that called for by the equation. The vapor tension at -111.8° was 226 mm. Although the same quantity of methylethyl ether is called for, only 1.93 mmoles or 79.3 per cent of the theoretical was obtained. The remaining 0.49 mmol probably stayed behind in the reaction bulb in combination with some of the $Al(BH_4)_2OC_2H_5$. Aluminum borohydride forms stable etherates of low volatility, the diethoxy borohydride does not form etherates stable at room temperature; it is reasonable to assume that the monoethoxy derivative would be intermediate between these in this respect.

Although the amount of diborane obtained agrees exactly with that expected if $Al(BH_4)_2OC_2H_5$ is the aluminum compound formed, and the deficiency in the quantity of ether liberated is satisfactorily explained, another experiment was carried out further to confirm the course of this reaction. In this case the reaction bulb was equipped with a magnetic breaker to facilitate the removal of slightly volatile products. After the reaction had taken place, the bulb was sealed to a high temperature vapor tension apparatus.[9] The diborane and ether were pumped out of

---

[9] A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc., 59, 785 (1937).

the system in the manner described above. By means of the hair dryer, the $Al(BH_4)_2OC_2H_5$ was distilled from the tail of the bulb to the upper surfaces where it crystallized. A water bath was then placed around the reaction bulb and slowly heated. The compound melted at 47°C. It was then distilled into the vapor tension apparatus. The vapor tension was measured and found to be 1 mm at 30° and 2 mm at 50°. The compound decomposes at temperatures above 50°, yielding hydrogen and an unidentified solid.

Some of the aluminum monoethoxy borohydride was then distilled into a reaction tube and hydrolyzed. The hydrogen evolved was measured by water displacement.

Weight of sample - 0.1680 gm. - 1.65 mmol

H_2 calculated for hydrolysis - 13.22

H_2 obtained - 12.75

The error in these results--4 per cent--is within the probable error for the hydrolysis apparatus employed.

The Reaction of Aluminum Borohydride with Methylal.

$$2Al(BH_4)_3 + 2H_2C(OCH_3)_2 \longrightarrow 2CH_3OCH_3 + B_2H_6 + 2Al(BH_4)_2OCH_3$$

A mixture of 4.46 mmoles of aluminum borohydride and 4.39 mmoles of methylal was allowed to warm slowly from liquid nitrogen temperature. Before room temperature was reached a reaction began as made evident by the formation of a cloud which condensed to drops of a viscous liquid. The latter was easily distilled to a part of the apparatus cooled with liquid nitrogen where it condensed to a solid deposit.

The volatile products were separated from the residue and from each other by the procedures used and described in connection with the preceding experiments. The more volatile material consisted of diborane and methyl ether, in agreement with the reaction

equation suggested, but the amounts fell short of those expected. The quantity of diborane was 1.91 mmoles instead of 2.20 mmoles, or 87 per cent of theoretical; the quantity of dimethyl ether (3.31 mmoles) was only 75 per cent of theoretical. The deficiency in diborane is probably due to failure of the reaction to procede to completion; the greater deficiency in the ether is undoubtedly due to compound formation of the ether with the less volatile reaction product, as discussed in connection with the preceding experiment.

As in the preceding case, the less volatile residue consisted of a portion that could be slowly sublimed to cooler portions of the apparatus where it condensed to crystals like those characteristic of $Al(BH_4)_2OC_2H_5$; there was also a solid which could not be sublimed without decomposition and which is probably the etherate of the aluminum monomethoxy borohydride.

The Reaction of Aluminum Borohydride with Chloroform.

$$6CHCl_3 + 2Al(BH_4)_3 \longrightarrow 6CH_2Cl_2 + 3B_2H_6 + 2AlCl_3$$

An excess (16.46 mmoles) of chloroform was added to aluminum borohydride (4.37 mmoles), and the mixture allowed to stand in a sealed reaction vessel for 2 days at room temperature, by which time a considerable quantity of a white solid had collected. The volatile material was then removed and fractionated by the procedures previously described. The condensate in the -195° trap consisted of 5.52 mmoles of almost pure diborane (vapor tension at -111.8°C., 222 mm); the material in the -140° trap was refractionated through -65° and -80° traps. The latter fraction was once more fractionated through a -80° trap and found to be methylene chloride (vapor tension at 0° and 25° were 149 and 445 mm, respectively, as compared to reported values[10] of 148 and 445

---

[10]International Critical Tables, 3, 215 (1928).

mm. Judging from the quantity of diborane obtained (85 per cent of the theoretical), the reaction, which was observed to be slow, had not gone to completion. Results obtained when an excess of aluminum borohydride was used showed that under these conditions also the only volatile products are diborane and methylene chloride.

Reaction of Aluminum Borohydride with Methyl Iodide.

$$2Al(BH_4)_3 + 6CH_3I \rightarrow \begin{cases} 6CH_4 + 3B_2H_6 + 2AlI_3 \\ 3(CH_3)_2B_2H_4 + 6H_2 + 2AlI_3 \end{cases}$$

Methyl iodide and aluminum borohydride react slowly at room temperature and more rapidly at 60° to yield the same products. However, the products are obtained in different proportions at the two temperatures. At room temperature, 79 per cent of the carbon is found as methane and 21 per cent as methylated diborane, while at 60° the proportions are 65 per cent and 35 per cent.

Experiment A--Reaction at Room Temperature. Methyl iodide, 8.70 mmoles, and aluminum borohydride, 2.89 mmoles, were sealed in a tube equipped with a side arm and were allowed to stand at room temperature. After three days, the liquid had all disappeared and white cubic crystals had formed. The reaction tube was sealed to the vacuum line and the gases not condensable at -195° were removed with a Toepler pump and measured. A mixture of hydrogen and methane (8.43 mmoles) was obtained. The presence of methane was indicated by the fact that the pressure in the system being evacuated with the Toepler pump fell rapidly to about 15 mm, and then remained at that value while a considerable volume of gas was removed. In another experiment, the molecular weights of various fractions of the gas were determined and found to vary from 7.3 to 15.1.[11]

---

[11]The more volatile hydrogen is first removed; it is for

The volatile products which were condensable at -195° were removed by evacuation through a U-tube cooled with liquid nitrogen The non-volatile solid remaining in the reaction tube was weighed, dissolved in water and analyzed for aluminum by precipitation with 8-hydroxyquinoline and for iodine by precipitation with silver. The results gave 2.86 mmoles of aluminum and 8.31 mmoles of iodine, as compared with the 2.83 and 8.50 mmoles calculated from the equation. The ratio of aluminum to iodine (1.00/2.97) confirms the formation of aluminum iodide.

The volatile material trapped at -195° contained diborane and dimethyl diborane. A procedure first used by Schlesinger and Brown[12] was employed to determine the relative quantities of the diborane and methyl diboranes. The mixture of diborane and dimethyl diborane (4.41 mmoles) was treated with an excess (10.51 mmoles) of trimethyl amine in a 500 ml bulb. The excess trimethyl amine (1.90 mmoles) was removed by evacuation through traps at -80° and -195°, in the latter of which the trimethyl amine was condensed. Since one molecule of trimethyl amine is used for each atom of boron present, the amount of boron present in the sample was 8.61 mmoles. The quantity which is called for by the equation (calculated on the basis of the aluminum boronydride used) is 8.67 mmoles. The material formed by the interaction of the amine and the boron compounds was hydrolyzed and gave 24.00 mmoles of hydrogen. Thus the CH_3 present was 3 x 8.61 - 24.00 = 1.83 mmoles This corresponds to 0.92 mmol of dimethyl diborane. The reaction therefore proceeds at room temperature 78.8 per cent to form methane and 21.2 per cent to form dimethyl diborane.

---

this reason that the earlier samples of the material removed by the Toepler pump have the lower molecular weight.

[12] H. I. Schlesinger and H. C. Brown, J. Am. Chem. Soc., 62, 3433 (1940).

Summary of Experiment:

Used

CH_3I: 195.2 cc (S. C.) or 8.70 mmoles

$Al(BH_4)_3$: 64.9 cc (S. C.) or 2.89 mmoles

Products	Found	Calc. from Equation on Basis of $Al(BH_4)_3$
$CH_4 + H_2$[13]	8.43 mmoles	8.68 mmoles
$B_2H_6 + (CH_3)_2B_2H_4$[13]	4.41	4.33
AlI_3	2.86	2.89

Experiment B--Reaction at 60°: An 8.72 mmol sample of methyl iodide was sealed off in a tube together with 2.90 mmoles of aluminum borohydride and heated to 60° overnight. The tube was then opened and the non-condensable material formed was removed with a Toepler pump and measured. A mixture of hydrogen and methane (8.09 mmoles) was obtained. The diborane and dimethyl diborane were removed as in the previous experiment. After the remaining solid had been weighed, it was dissolved in methanol; the reason for treating the residue with methanol instead of with water is that the aluminum borohydride at 60° undergoes slow decomposition to a non-volatile product which reacts violently with water. Actually gas evolution occurred when the methanol was added, thus indicating that some of the decomposition product referred to had been formed.

Used

CH_3I: 195.5 cc (S. C.) or 8.72 mmoles

$Al(BH_4)_3$: 65.0 cc (S. C.) or 2.90 mmoles

---

[13]It is seen that, according to the postulated equations, the sum of the number of moles of methane and hydrogen remains 3 times the number of moles of aluminum borohydride used, irrespective of the quantities of these products relative to each other. For diborane and dimethyl diborane the sum should equal 3/2 of the number of moles of aluminum borohydride.

Found		Theoretical
$H_2 + CH_4$[14]	181.5 cc (S. C.) or 8.09 mmol	8.72 mmol
$B_2H_6 + (CH_3)_2B_2H_4$[14]	107.7 cc (S. C.) or 4.80 mmol	4.68
AlI_3[14]	1.093 gm or 2.68 mmol	2.69

In another experiment, an attempt was made to separate the diborane and dimethyl diborane quantitatively by distillation. The total quantity of the mixture used was 4.05 mmoles. On distillation through a -140° trap three times, 2.63 mmoles of diborane which was still impure (vapor tension at -111.8°, 203 mm) was obtained. If this is considered a maximum value for the diborane fraction, the reaction at 60° can be estimated to have gone 65 per cent to methane and 35 per cent to methyl diborane.

The Reaction of Aluminum Borohydride with Methylene Fluoride.

$$6CH_2F_2 + 4Al(BH_4)_3 \begin{cases} \nearrow 6CH_4 + 6B_2H_6 + 4AlF_3 \\ \searrow 3(CH_3)_2B_2H_4 + 3B_2H_6 + 6H_2 + 4AlF_3 \end{cases}$$

Two experiments were carried out. In the first, 2.07 mmoles of methylene fluoride and 1.38 mmoles of aluminum borohydride were heated together in a sealed tube to 60° for about 14 hours, during which time a white solid had coated the inner surface. The non-condensable material (42.2 cc or 1.88 mmoles) had an average molecular weight of 9.7, corresponding to a mixture of 55 per cent of methane and 45 per cent of hydrogen. The material condensable at -195° was fractionated through U-tubes at -111.8°, -120°, -140° and into one at -195°C.[15] The last fraction

---

[14]The fact that the observed quantity of hydrogen + methane is less than theoretical, whereas that of diborane + dimethyl diborane is higher, is readily explained by the slight decomposition of the aluminum borohydride already referred to. As a result, not all of the methyl iodide reacted and the unchanged portion remained behind with the mixture of diborane and methyl diboranes.

[15]Method of H. I. Schlesinger and A. O. Walker, J. Am.

consisted of impure diborane (vapor tension at -111.8°, 200 mm instead of 225 mm). The -120° fraction was identified as dimethyl diborane by its 10 mm vapor tension at -78.5°C., a value identical with that observed by Schlesinger and Walker.[15] Judging from the volume of the combined hydrogen and methane fraction, the reaction had gone 91 per cent to completion.

In another experiment, a mixture of 8.88 mmoles of methylene fluoride and 6.01 mmoles of aluminum borohydride was heated in a sealed flask of 500 cc capacity for 16 hours at 55°. At the end of that time, there had been formed 3.16 mmoles of non-condensable gas with an average molecular weight of 12.4, corresponding to 2.35 mmoles of methane and 0.812 mmoles of hydrogen. The remaining material was recondensed into the reaction flask, which was resealed and heated at 55° for another 36 hours. The non-condensable reaction product was this time removed in two portions, one of 91.4 cc and one of 46.7 cc (S. C.). The former had an average molecular weight of 5.5, corresponding to 25 per cent of methane and the latter an average molecular weight of 15.7 or methane of 98 per cent purity.[16] The total amount of methane was 5.11 mmoles, that of hydrogen 3.91, or 9.02 mmoles together instead of the 8.88 to be expected from the equation. The slight excess may readily be accounted for on the assumption that it consisted of hydrogen resulting from thermal decomposition of aluminum borohydride. Correction for this amount of hydrogen (0.14 mmoles) leads to the ratio 57.5/42.5 for the methane-hydrogen ratio.

Chem. Soc., 57, 624 (1935) for the separation of diborane from its methyl derivatives.

[16] It is to be expected that the second fraction be rich in methane since the latter is removed from a mixture of liquids and vapor more slowly than hydrogen.

The Reaction of Aluminum Borohydride with Methylene Iodide.

$$6CH_2I_2 + 4Al(BH_4)_3 \longrightarrow 3(CH_3)_2B_2H_4 + 3B_2H_6 + 6H_2 + 4AlI_3$$

A mixture of methylene iodide (9.67 mmoles) and aluminum borohydride (1.46 mmoles) was heated overnight at 60°, after which time the accumulated non-condensable material was removed and found to measure 220 cc (S. C.) or 9.80 mmoles. The quantity of gas corresponded satisfactorily to that demanded by the equation. Because of the small size of the sample, the molecular weight determination was unsatisfactory; its low value (1.05) indicated that methane was absent. The material condensable at -195° was fractionated through a series of U-tubes at -45°, -140° and -195°, respectively. The -195° fraction had a vapor tension of 190 mm, a value considerably below that for pure diborane. The -140° fraction was redistilled through a series of U-tubes at -111.8°, -120°, and -195°. The middle fraction had vapor tensions of 10 mm at -78.5° and of 105 mm at -45°. The values of Schlesinger and Walker[15] for dimethyl diborane for these temperatures are 10 and 103 mm, respectively.

To verify the conclusion that methane was absent, a second experiment, involving 22.0 mmoles of methylene iodide and 14.4 mmoles of aluminum borohydride, was carried out. The mixture was heated at 55° for 38 hours, yielding 440 cc (S. C.) of non-condensable gas, or 19.6 mmoles. The gas density of this material corresponded to a molecular weight of 2.26 which, considering that the weight of the sample measured was only 7 mg, is in satisfactory agreement with that of hydrogen. In order to identify diborane more satisfactorily than in the first experiment, the volatile residue was fractionated twice through a -150° trap; the material condensed at -195° had the vapor tension of diborane (225 mm at -111.8°).

The results of the two experiments confirm the conclusion that the products of the reaction are hydrogen, diborane and methyl diboranes (chiefly dimethyl diborane), and that no methane is formed. The reaction in the first experiment apparently went to completion, in the second the yield was about 88 per cent.

The Reaction of Aluminum Borohydride with Ethylene Bromide.

It was found in a preliminary experiment that ethylene bromide and aluminum borohydride react with a flash of flame at room temperature after a long induction period. An attempt was made to control the reaction by the addition of aluminum borohydride to the ethylene bromide in small quantities. Even this procedure was not entirely successful and a red glow was observed in the reaction tube as the reaction took place. A considerable amount of brown material was deposited on the walls of the reaction tube.

The non-condensable material was removed with a Toepler pump in three portions; the first had a molecular weight of 1.8, the second 6.1, and the third 15.1. The vapor tension of the last portion was 15 mm at -195°. These facts indicate that the non-condensable material consisted of hydrogen and methane.

The remaining volatile materials were distilled through a -140° trap. The fraction passing through had a -111.8° tension of 205 mm and could contain diborane, ethane or monomethyl diborane. Since ethane and diborane cannot be separated by fractional condensation, another procedure was employed. The material (6.55 mmoles) was allowed to stand over pyridine for 2 hours. The diborane (2.63 mmoles) was absorbed to form pyridine borine. The remaining material had a vapor tension of 177 mm at -111.8°, a value which agrees with that reported for ethane. The products of the reaction thus appeared to be methane, ethane, diborane,

and, very probably, some methyl diboranes. Because the violence of the reaction led to the formation of solid unidentifiable decomposition products, it seemed pointless to attempt the complicated separation of the various volatile products or to attempt a formulation of the reaction.

The Reaction of Aluminum Borohydride with Phosgene.

$$3COCl_2 + 2Al(BH_4)_3 \longrightarrow 3CO + 3H_2 + 3B_2H_6$$

Phosgene and aluminum borohydride also react violently. The best results in controlling the reaction were obtained with the following procedure: the aluminum borohydride was added in small portions to the phosgene. The mixture was carefully warmed until the reaction became vigorous, at which time a liquid nitrogen bath was applied. By alternate warming and cooling, the reaction was allowed to proceed to completion. The non-condensable material formed in each step was removed by evacuation, more aluminum borohydride was added, and the procedure was repeated. The average molecular weight of the non-condensable mixture obtained was 5.3, a value which suggests that hydrogen, and probably carbon monoxide were present.

Diborane was isolated from the products by distillation of the volatile material through a -160° trap. The vapor tension at -111.8° was 225 mm. There was also found some material which was less volatile than diborane, and which decomposed to non-condensable gas on standing at room temperature. This behavior suggests borine carbonyl. The conditions of the reaction were not those best suited for the production of borine carbonyl, but the formation of a small amount might be expected.

SUMMARY

1. The reactions of a number of alkoxy and halogen derivatives of carbon toward aluminum borohydride have been investigated. The alkoxy derivatives, ethyl orthoformate and methylal give methylethyl and dimethyl ether, respectively. Chloroform gives methylene chloride and diborane. Methyl iodide and methylene fluoride produce diborane, methyl diboranes, methane, and hydrogen; these same products with the exception of methane result from the reaction of methylene iodide on aluminum borohydride. The reactions of methylene bromide and of phosgene were violent. In the former case methane, ethane, and diborane were identified among the reaction products, methyl diboranes were probably formed, but unidentifiable solids were also present; phosgene produced diborane and probably carbon monoxide. Methylene bromide, methylene chloride, iodoform, carbon tetrachloride and carbon tetrafluoride do not react.

2. The differences in the nature of the products obtained from organic compounds, which are in many other respects quite alike, are pointed out, and are systematized by the assumption that the controllable reactions have proceeded through the formation of an intermediate carbon borohydride which immediately decomposes by loss of borine, or of hydrogen, or of both. The logical difficulties which stand in the way of accepting this assumption as an actual reaction mechanism are discussed in detail.